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The effect of high pressure on MOF-5: Guest induced pore size and content modification at pressure**

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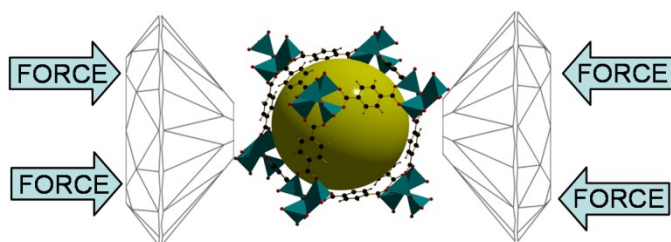
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Graphical abstract:



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Abstract

Here we report the first high-pressure crystallographic study on the metal organic framework MOF-5. Increasing pressure initially results in the pressure transmitting fluid being squeezed into the pores. Further pressure increases causes a large reduction in pore content as solvent is evacuated from the pores, until a complete loss of crystallinity is observed at pressures above 3.2 GPa.

Main text

Recent interest in gas storage materials has led to the accumulation of a large volume of work on the physical properties and possible applications of metal organic framework (MOF) materials. These studies have utilized a number of techniques to probe the mechanical properties of MOFs including nanoindentation, computation and high-pressure crystallographic techniques.¹⁻³ Previous work includes high-pressure crystallographic studies on the dense zeolitic imidazolate framework (ZIF) material ZnIm ([Zn(Im)₂], Im = imidazole),⁴ the copper framework HKUST-1 ([Cu₃(TMA)₂(H₂O)₃]_n,⁵ TMA = benzene-1,3,5-tricarboxylate) and ZIF-8 [Zn(MeIM)₂, MeIM = 2-methylimidazolate].⁶ In these studies GPa pressures were generated using a diamond anvil cell (DAC). This involves placing a crystalline sample into a gasket chamber between two opposing diamond anvils and surrounding the sample with a pressure-transmitting medium (usually a gas or liquid) in order to apply pressure evenly to the sample. In both HKUST-1 and ZIF-8 some of the pressure-transmitting medium entered the pores, resulting in guest-dependent pressure behaviour for HKUST-1, while guest induced-pore size and content modification (including a guest-driven phase transition) was observed for ZIF-8.

Here we present the first reported high-pressure study on the prototypical MOF, MOF-5 [Zn₄O(BDC)₃, BDC = 1,4-benzenedicarboxylate] to 3.2 GPa. MOF-5 crystallizes in the cubic space group *Fm-3m*. The structure is composed of an oxide-centred Zn₄O tetrahedron edge-bridged by six carboxylate groups which create an octahedral secondary building unit (SBU). These SBUs build up to give a three dimensional porous network with each pore having a volume of *ca.* 1600 Å³ (Figure 1a).

In this study a single crystal of MOF-5 was loaded into a Merrill-Bassett DAC equipped with 600 μm culets and a tungsten gasket (Figure 1b) and surrounded with diethyl formamide (DEF) as the pressure-transmitting medium. This was used preferentially over other mediums (*e.g.* alcohols), as exchange with other more volatile solvents caused the single crystal to become polycrystalline. This MOF-5 sample is hereafter called MOF-5DEF to reflect its solvent content. High-pressure data were collected on station I19 at the DIAMOND Light Source in approximately 0.5 GPa steps between 0.3

and 3.2 GPa. Pore volume and solvent content were calculated using the SQUEEZE algorithm within PLATON (see ESI).⁷

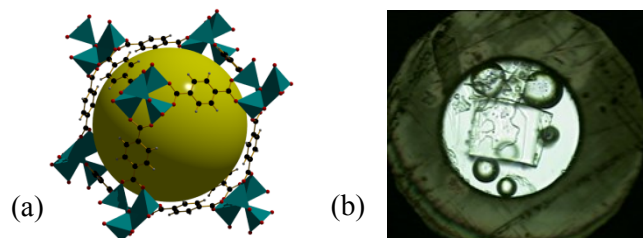


Figure 1. (a) Packing arrangement demonstrating the pore structure of MOF-5. ZnO_4 units are drawn as rigid polyhedra. The large sphere represents the largest van der Waals sphere that would fit in the cavity without touching the framework. There are eight of these units per unit cell. (b) Optical image of a single crystal of MOF-5 at 0.3 GPa in a diamond-anvil cell.

Our first measurement at 0.3 GPa showed that the pores contained 119 DEF molecules per unit cell. On initial application of pressure to 0.8 GPa, a rather counterintuitive unit cell volume *increase* of 144 \AA^3 was observed and coincided with a moderate solvent content increase (9 DEF molecules, Table 1). Initial application of pressure therefore resulted in solvent being squeezed into the pores, making the framework resilient to compression. Although this action does result in a slight increase in pore volume, the change here is very modest (ca. 0.8%) but still statistically significant.

Pressure (GPa)	a (\AA)	Total Pore Volume (\AA^3)	Electron Count	DEF Molecules
0.3	25.761(6)	13020	6667	119
0.8	25.832(8)	13221	7175	128
1.3	25.732(6)	12962	4163	74
1.5	25.656(11)	12893	4217	75
1.7	25.626(8)	12825	4053	72
2.0	25.587(15)	12936	3947	70
2.3	25.40(3)	12415	3739	67

Table 1. Crystallographic and pore data for MOF-5DEF as a function of pressure.

On further increasing the pressure to 1.3 GPa the volume finally began to decrease, although we note that the volume here at *ca.* 13000 atmospheres is almost identical to that at 0.3 GPa. What is not immediately obvious on the basis of the unit cell volume alone is that a marked and sudden *decrease* in solvent content (42 %) occurs as the DEF is now squeezed out of the pores. Increasing pressure further to 3.2 GPa resulted in behavior atypical to molecular materials under pressure, with a gradual

and steady reduction in volume. Three regions could therefore be identified, the first (0.3-0.8 GPa) involves inclusion of DEF into the pores, the second (0.8-2.0 GPa) resulted in compression and evacuation of the framework, rather than the uptake of more solvent, while the region above 2.0 GPa and beyond to 3.2 GPa resulted in a sharper drop in unit cell volume, and compression of the framework.

During the pressure experiment, the single crystal began to shatter, becoming polycrystalline, while a gradual reduction in resolution of the data was observed, reducing from 0.9 to 1.7 Å. Due to the decrease in resolution, atomic coordinates could only be refined reliably to 2.3 GPa, although unit cell dimensions could be determined up to 3.2 GPa. At pressures above 3.2 GPa the sample became completely amorphous, making extraction of structural data by these techniques impossible. Amorphisation was followed by mapping the intensity of the (022) reflection as a function of pressure, and is included in the ESI. The reversibility of this process is currently unknown.

Amorphisation at pressure has been observed in the porous framework ZIF-8 using a pressure-transmitting media which was non-penetrating into the pore,⁸ and has also been reported for MOF-5 during grinding experiments by Hu *et al.*⁹ In this work samples were ground for 30 minutes and then subjected to (ambient pressure) powder X-ray diffraction measurements. Although amorphisation of MOF-5DEF is eventually observed in our study, it is at pressures several orders of magnitude higher than that observed by Hu and co-workers. Although the hydrostatic limit of DEF is currently unknown, and the onset of amorphisation could be caused by applying pressures above this limit, it does appear that applying pressure using a hydrostatic fluid that can penetrate into the framework stabilises MOF-5 to external pressure thereby delaying the onset of amorphisation of the sample.

The fact that we observed unit cell volume expansion under modest conditions of pressure in the presence of a small-molecule solvent requires further investigation. Nevertheless, de-convoluting the effect of pressure and solvent inclusion/exclusion as a function of pressure is extremely difficult to achieve. In a previous high-pressure study of HKUST-1 this was achieved by surrounding the sample with a pressure transmitting medium that was too large to enter the pores.⁵ Direct compression of the framework was then observed, although no detailed structural data was obtained. Similar experiments cannot be performed on MOF-5 because of the size of the cavities. The diameter of the channels at 0.3 GPa measures around 7.6 Å,¹⁰ and have previously been shown to be large enough to encapsulate (and separate) organic dyes.¹¹ In order to establish the effect of solvent inclusion, we therefore turned to density functional theory (DFT) calculations to simulate the effect of pressure on the unit cell volume of MOF-5 in the absence of the pressure-transmitting medium (hereafter referred to as MOF-5Evac, see ESI for details). Our starting model for the computational study was the ambient pressure, 30 K X-ray diffraction structure of MOF-5 by Rowsell *et al.*¹² Our optimized structure returned Zn-O bond lengths that were slightly longer (approx. 0.02 Å) at ambient pressure than the experimental study, which in turn leads to a slightly larger calculated lattice parameter. MOF-5 is unusual in that it shows quite a large variation in volume under ambient pressure conditions, ranging from 16913.2(3) Å³ (for a completely de-solvated sample at 213K) to 17369.9(1) Å³ (for an N₂ containing material at 30K).^{12, 13} In-fact, MOF-5 has previously demonstrated negative thermal expansion behaviour.¹⁴ It is therefore unsurprising that the calculated values at ambient pressure determined here are larger than the 30K experimental data. Nevertheless, the calculated geometrical data are within 2.6 % of the experimental values and correlate closely with a previous *ab initio* study by Civalleri *et al.*,¹⁵ which helps to validate the computational approach.

In previous computational studies of MOF-5, the bulk moduli (*K*), which is a measure of the compressibility of the material was calculated, and found in the range 16.3-18.5 GPa.¹⁶⁻¹⁹

Reassuringly, we calculate a K value of 16.52 GPa for our computational study, which corresponds well with these previous studies.²⁰ To date, our study on MOF-5DEF is the only experimental data available on the effect of high pressure on MOF-5. The bulk modulus for MOF-5DEF, however is much harder to estimate as pore filling and evacuation of solvent from the framework is a pressure-dependent process. In order to compare our experimental results to the calculated compression (and value of K) of the evacuated framework, an ambient temperature and pressure data set was required of a DEF containing MOF-5 crystal prior to collecting data (on the same sample) at high-pressure. This was achieved by mounting another single-crystal of MOF-5 using a MiTeGen Microloops™ mount with DEF solvent supported above the crystal in a capillary. The same crystal was then loaded into a Merrill-Bassett DAC (as above) and pressure data were collected to 3.2 GPa on a Bruker ApexII 3-circle goniometer with MoK α radiation. Only unit cell parameters could be extracted from these data (Figure 2). Comparisons of laboratory and synchrotron data are included in the ESI.

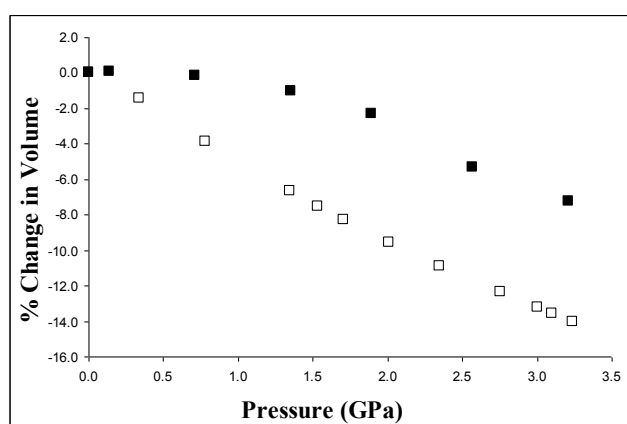


Figure 2. Percentage change in volume for laboratory MOF-5DEF data (filled squares) and MOF-5Evac derived from the computational analysis (empty squares) as a function of pressure.

As the pressure is increased, the difference between MOF-5DEF and MOF-5Evac is obvious: the absence of solvent results in the framework contracting by around 3 % (Figure 2). Increasing the pressure further shows a significantly greater reduction in volume on compression of the evacuated framework. Quantifying the rate of change of the experimental data proved impossible to fit using universal Vinet or Birch-Murnighan equation of states, without giving very large uncertainties on the parameters, yielding unphysical values for both K , and its first derivative, K' (the pressure dependence of K). This is unsurprising due to both the initial expansion and subsequent contraction of the framework. The best that could be achieved was to estimate the bulk modulus by finite difference, which drops rapidly from 242 GPa (0.1 to 0.7 GPa) to values between 20-40 GPa at higher pressure. The bulk modulus as a function of pressure has been included in the ESI. This is a remarkable difference in compressibility. To put this into perspective, some examples of K include 25 GPa for NaCl, 37 GPa for quartz (a soft mineral), and 440 GPa for diamond. Clearly these much higher values can be attributed to the pore filling mechanism recognized in the lower pressure regime which significantly decreases the compressibility of the material.

Previous high-pressure work on amino acids has shown that covalent bonds do not compress within this pressure regime.²¹ Metal-ligand bond distances are however much more amenable to pressure

modification, including pressure-induced co-ordination changes.²² Here, we observe that the compression of MOF-5 is mediated through the Zn-O bonds. Because of the high-symmetry of the complex, there are only two symmetry independent Zn-O bond distances, labeled Zn-O1 and Zn-O2. These bonding interactions are to a μ_4 -oxygen atom (O1) which sits at the centre of the Zn_4O_{13} cluster, and a carboxyl oxygen atom, (O2) (Figure 3).

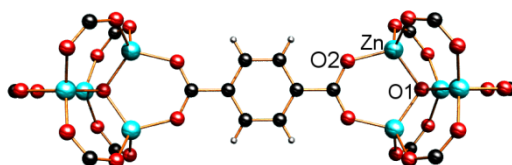


Figure 3. Axial component of MOF-5 comprising a terephthalic acid moiety bordered by Zn_4O_{13} fragments. The two symmetry independent Zn-O bonds, Zn-O1 and Zn-O2, are shown.

On increasing pressure the displacement parameters of all the atoms increased in size. In previous studies of MOF-5 as a function of temperature, thermal motion of the BDC ligand gave rise to negative thermal expansion of the framework. The increase in the anisotropic displacement parameters here however, is a consequence of the reduction in resolution of the data. Nevertheless, in order to remove the possibility of any libration effects on measured Zn-O bond lengths we performed TLS analysis on the $\text{ZnO}(\text{CO}_2)_{12}$ unit and correspondingly corrected all Zn-O bond lengths (Figure 4). The effect on calculated bond lengths here was small, and details of this analysis as a function of pressure are given in the ESI.

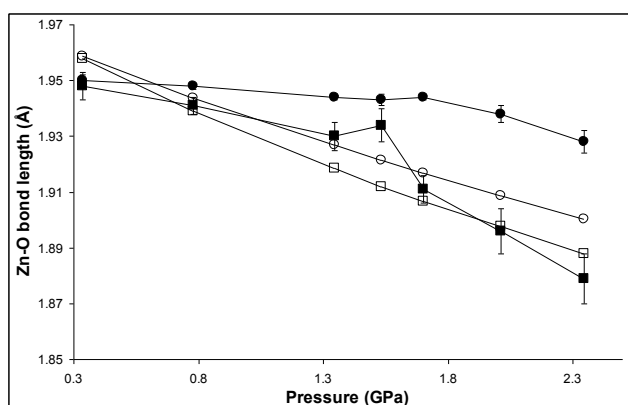


Figure 4. Variation in Zn-O1 (circles) and Zn-O2 (squares) bond lengths in MOF-5DEF and MOF-5Evac as a function of pressure. Filled and empty data points refer to MOF-5DEF and MOF-5Evac (derived from the computational analysis) respectively.

On comparing the variation in length of Zn-O1 and Zn-O2 over the entire pressure regime in MOF-5DEF and MOF-5Evac, it becomes clear that these bonding interactions do not have the same compressibility. The low pressure region (0.3 to 0.8 GPa) corresponds to solvent inclusion in MOF-

5DEF and contraction in MOF-5Evac, with a cross-over point at around 0.8 GPa where the two Zn-O bond lengths are measured, and calculated, to fall within a narrow range. Across the whole experimental data set Zn-O1 shows little variation with pressure. Most of the structural variation is found for Zn-O2. Thus it would appear that it is the Zn-O2 distance that accommodates most of the compression in MOF-5 during the higher pressure region as the pores contract. The Zn-O bonding interaction (Zn-O1) to the μ_4 -oxygen atom is therefore significantly stiffer than the Zn-carboxylate bond (Zn-O2). EXAFS and total scattering studies would be useful here for tracking bond compression. These techniques are however still being developed at high-pressure and we plan to try these in the future.

In a previous *ab initio* study of MOF-5, born effective charges showed that the μ_4 -oxygen atom O1 had a greater negative charge than the carboxyl oxygen atom O2 by around $-0.4 e$,¹⁵ a finding that was matched by calculated Mulliken charges in this study. The different nature of the two atoms was also highlighted in the same study by a deformation electron density map, which clearly showed that the O1 atom was similar to the oxygen atom in ZnO wurtzite, while the Zn-O2 bond was clearly formed by charge donation from the oxygen atom. It is therefore not surprising that the Zn-O2 bond is the more compressible of the two bonds, with the high-pressure study here providing an effective proof for this observation. In the simulation, both Zn-O1 and Zn-O2 bonds display a steady compression (of the order of 0.05 and 0.06 Å, respectively). Interestingly, the greater compressibility of Zn-O2 is still observed in the evacuated framework, though not to the same extent. This would indicate that solvent inclusion in MOF-5DEF makes the Zn-O1 (μ_4 -oxygen) bond even stiffer. At the moment, it is unclear as to why this would be the case and we are currently investigating this phenomenon.

In conclusion, we have observed the effect of pressure on the metal organic framework MOF-5 from ambient to 3.2 GPa, and subsequently explored what drives the framework's behavior. Initial compression to 0.8 GPa represents a pressure region where solvent is 'squeezed' into the pores. This is highlighted by comparison with computational results which show direct compression of the evacuated framework. Increasing the pressure further to 1.3 GPa results in a decrease in volume and a sudden marked decrease in solvent content as the solvent is evacuated from the pores. Increasing the pressure to 3.2 GPa resulted in a gradual and steady reduction in volume and resolution of the data as the sample became amorphous. Increasing pressure above 3.2 GPa resulted in complete amorphisation of the sample. When compared with a previous high-pressure study it appears that hydrostatic compression delays the onset of amorphisation.⁹ This indicates that pressure-induced solvent inclusion makes the framework more resilient to pressure. Compressibility of the framework is mediated through Zn-O bonds. In particular, the Zn-O2 bond (to the carboxyl oxygen atom) shows significantly greater compression than the Zn-O1 bond (to the μ_4 -oxygen atom). This is also observed in the computational results on the evacuated framework, though interestingly the Zn-O1 bond here compresses significantly more. How the presence of solvent effects the compressibility of Zn-O bonds is still under investigation.

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